PATENT ABSTRACTS OF JAPAN

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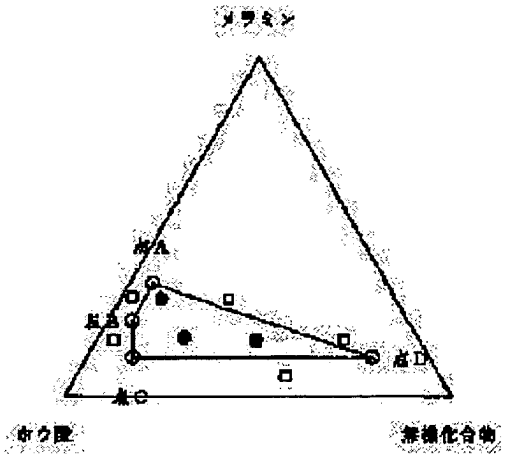
(54) BORATE PARTICLE, PRODUCTION OF INORGANIC POWDER CONTAINING THE PARTICLE, AND ITS USE

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain Mg or Ca borate particles having high thermal conductivity, large electric insulating property and excellent heat radiating property by coating the particles with hexagonal boron nitride.

SOLUTION: A mixture of melamine, boric acid and inorg. compds. selected from hydroxides and carbonates of Mg and Ca is used as the starting material. The compsn. of the mixture ranges in the area in the ternary compsn. diagram by molar percentages defined by lines connecting the points A(35, 60, 5), B(25, 70, 5), C(5, 80, 15) and D(5, 5, 90). The source material mixed in a ball mill or the like is kept in an atmosphere at 40 to 100°C and >5% relative humidity for 1 to 100 hours to produce a mixture containing melamine borate and hydroxides and/or carbonates of Mg and/or Ca. The mixture is compacted under pressure preferably of ≤ 100 kgf/cm2, and calcined in a nonoxidizing atmosphere such as nitrogen at 1,700 to 2,000°C for 2 to 10 hours to obtain mixture powder containing hBN-coated borate particles and boron nitride particles. The obtd. powder is suitable as a filler for a heat radiating member of electronic parts.



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* NOTICES *

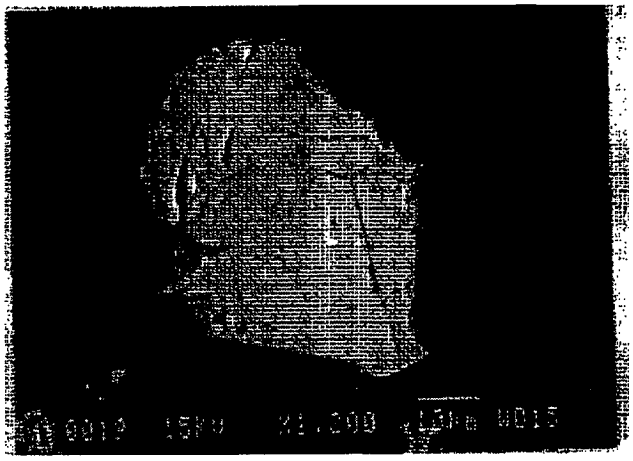
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] The borate particle of the magnesium characterized by coming to be covered with hexagonal boron nitride, or calcium.
[Claim 2] The borate particle according to claim 1 characterized by the area pulse duty factor of the borate part observed in the particle cross section by the electron microscope (SEM) being 10 - 80%.
[Claim 3] The borate particle according to claim 1 characterized by the coverage by hexagonal boron nitride being 80% or more.
[Claim 4] Mixed powder which consists of mixture of the borate particle of hexagonal boron nitride covering according to claim 1, 2, or 3, and a boron nitride particle, and is characterized by the ratio (I002/I100) of the diffraction reinforcement I002 of the field (002) of boron nitride and the diffraction reinforcement I100 of a field (100) by powder X diffraction measurement being 100 or less.
[Claim 5] Inorganic powder according to claim 4 characterized by a diffraction intensity ratio (I002/I100) being 50 or less.
[Claim 6] Radiator material characterized by making resin and/or rubber come to carry out a borate particle according to claim 1 or mixed powder according to claim 4 20-80 volume % content.
[Claim 7] The inorganic compound more than a kind chosen as the melamine, the boric acid, and the list from the hydroxide and carbonate of magnesium and calcium In the 3 yuan composition diagram (a melamine, a boric acid, inorganic compound) of mole percentage Points A (35, 60, 5), B (25, 70, 5), and C (5, 80, 15), The manufacture approach of the mixed powder containing the borate particle according to claim 1 characterized by mixing so that it may become within the limits surrounded by the line which connects D (5, 5, 90), and calcinating it at the temperature of 1700-2200 degrees C under a non-oxidizing atmosphere.
[Claim 8] The manufacture approach of the mixed powder according to claim 7 characterized by sorting out a particle 24 micrometers or more after baking.

[Translation done.]

Drawing selection Representative drawing



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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the process and application of the borate particle covered with hexagonal boron nitride, and the inorganic powder containing the particle.
[0002]
[Description of the Prior Art] A hexagonal boron nitride (henceforth "hBN") particle has the layer structure similar to a graphite, and the hBN powder which is the aggregate is excellent in properties, such as thermal conductivity, insulation, and chemical stability.
[0003] Then, in the electronic ingredient field, in order to carry out stripping of the heat generated from electronic parts efficiently, the radiator material which filled up resin or rubber with hBN powder, for example, heat dissipation grease, the high flexibility spacer, the heat dissipation sheet, etc. are used. Moreover, except the electronic ingredient field, it is used for a heat-resistant coating ingredient, an insulating rubber ingredient, covering material, the ingredient that has arc resistance, the neutron shielding material which uses B system compound, the lubricating grease for automobiles, oil, etc.
[0004] The usual hBN powder is the aggregate of a scale-like particle, if resin and rubber are filled up with this, in response to shearing stress, it will be cracked by the primary particle at the time of mixing and kneading, and particles will gather in the same direction (refer to JP,9-202663,A). (this phenomenon is hereafter called "orientation".) By this orientation, although the thermal conductivity of the direction of a field of a hBN particle (the direction of an a-axis) was 110 W/mK, that high temperature conductivity could not fully be made use of in radiator material, but thermal conductivity 2 W/mK of the thickness direction (the direction of a c-axis) of a particle was used.
[0005] For example, although the heat dissipation sheet was used as inclusion at the time of attaching electronic parts in a heat sink, since the thickness direction (the direction of a c-axis) will become the direction of a field of a heat dissipation sheet, and parallel and the orientation at the time of heat dissipation sheet production will be filled up with a hBN particle, it was not enough as radiator material of today's high febrility electronic parts.
[0006] Although thermally conductive improvement in radiator material is performed by raising the filling factor of hBN powder, if a filling factor is raised, since the flexibility and tensile strength of radiator material will be spoiled and orientation will also become remarkable, there is a limit in this approach.
[0007] Then, although use of the hBN powder (JP,9-202663,A) which controlled the granulation article of the hBN powder of the shape of a non-scale which cannot carry out orientation easily, for example, the hBN powder by spray drying, the grinding article of a hBN sintered compact, and the aggregate of a primary particle, and was manufactured was proposed, even if it was in these, in the engine performance and a price, it was not enough.
[0008]
[Problem(s) to be Solved by the Invention] This invention is made in view of the above, it is offering the inorganic big powder of high temperature conductivity and electric insulation, and the purpose is offering the radiator material excellent in the heat dissipation property.
[0009]
[Means for Solving the Problem] The summary of this invention is as follows.
[0010] (Claim 1) The borate particle of the magnesium characterized by coming to be covered with hexagonal boron nitride, or calcium.
(Claim 2) The borate particle according to claim 1 characterized by the area pulse duty factor of the borate part observed in the particle cross section by the electron microscope (SEM) being 10 - 80%.
(Claim 3) The borate particle according to claim 1 characterized by the coverage by hexagonal boron nitride being 80% or more.
[0011] (Claim 4) Mixed powder which consists of mixture of the borate particle of hexagonal boron nitride covering according to claim 1, 2, or 3, and a boron nitride particle, and is characterized by the

ratio (I002/I100) of the diffraction reinforcement I002 of the field (002) of boron nitride and the diffraction reinforcement I100 of a field (100) by powder X diffraction measurement being 100 or less.
(Claim 5) Inorganic powder according to claim 4 characterized by a diffraction intensity ratio (I002/I100) being 50 or less.
[0012] (Claim 6) Radiator material characterized by making resin and/or rubber come to carry out a borate particle according to claim 1 or mixed powder according to claim 4 20-80 volume % content.
[0013] (Claim 7) The inorganic compound more than a kind chosen as the melamine, the boric acid, and the list from the hydroxide and carbonate of magnesium and calcium In the 3 yuan composition diagram (a melamine, a boric acid, inorganic compound) of mole percentage Points A (35, 60, 5), B (25, 70, 5), and C (5, 80, 15), The manufacture approach of the mixed powder containing the borate particle according to claim 1 characterized by mixing so that it may become within the limits surrounded by the line which connects D (5, 5, 90), and calcinating it at the temperature of 1700-2200 degrees C under a non-oxidizing atmosphere.
(Claim 8) The manufacture approach of the mixed powder according to claim 7 characterized by sorting out a particle 24 micrometers or more after baking.
[0014]
[Embodiment of the Invention] Hereafter, with reference to the electron microscope (SEM) photograph of a substitution drawing, this invention is explained in more detail.
[0015] The SEM photograph of the high grade hBN particle (DENKI KAGAKU KOGYO K.K.) of again marketing of the cross-section SEM photograph of drawing 1 to drawing 2 was shown for the secondary electron image (SEM photograph) of the borate particle of hBN covering of this invention in drawing 1 and drawing 3 at drawing 4 . The borate of hBN covering of this invention is a massive particle, and, moreover, the structure is clearly different from the commercial hBN particle in the point which consists of the core section of the borate particle of magnesium or calcium, and the shell section which consists of the shape of a scale hBN which has covered the front face so that clearly from contrast with drawing 1 or drawing 3 , and drawing 4 . The check of the borate of magnesium or calcium and hBN can be performed using an energy dispersion mold fluorescence-X-rays measuring instrument.
[0016] The core section of the borate particle of hBN covering of this invention is acting as a crystallization catalyst at the time of manufacturing boron nitride powder from the raw material of a boric acid and a melamine. Since it becomes the particle which is hard to be cracked even if an orthoboric acid salt has high viscosity and it can moreover make hBN put on the front face firmly even if it is in such a borate, and it receives shearing stress, it is suitable for this invention. As for the rate of the core section, it is desirable that it is 10 - 80% in the area pulse duty factor of a particle cross section. The thing of drawing 2 is about 70%.
[0017] on the other hand -- the shell section (enveloping layer) of the borate particle of hBN covering of this invention -- the set object of the primary particle of the shape of a scale hBN -- it is -- the thickness -- number - it is desirable that it is about ten micrometers. Moreover, the shell section may be partially formed like drawing 3 , although it is optimal to form 80% or more of core section surface area in a wrap size like drawing 2 . In proportion to the coverage of the core section by the shell section, thermal conductivity becomes large.
[0018] Next, the mixed powder of this invention is the mixture of the borate particle of the above-mentioned hBN covering, and a boron nitride particle. A boron nitride particle here is a scale-like hBN primary particle. Although there is especially no limit in both mixed ratio, the rate that the ratio (I002/I100) (henceforth "OI value") of the diffraction reinforcement I002 of a field (002) and the diffraction reinforcement I100 of a field (100) analyzed by X-ray diffraction on condition that Table 1 in the green compact which cast mixed powder by the pressure of 100 kgf/cm2, and was obtained is 50 especially or less 100 or less is desirable. It is the description that this OI value is small to the conventional high grade hBN having been about several 100.
[0019] With the usual hBN powder, when a green compact is cast by the pressure of 100 kgf/cm2, a hBN primary particle carries out orientation within a green compact. On the other hand, since the borate particle by which the hBN particle was powerfully put on the borate front face is contained in the mixed

powder of this invention, even if a hBN primary particle may break away, there is little it and the orientation of the hBN particle within a green compact will become small.

[0020]

[Table 1]

Target	Cu
Filter	Ni
Voltage	30kV
Current	15mA
High Voltage	1350V
Time Constant	2秒
Scan Speed	2°/min (2θ)
Divergence Slit	1°
Receiving Slit	0.3mm
Scattering Slit	1°
Chart Speed	20mm/min

[0021] Although the manufacture approach of the mixed powder of this invention is mentioned later By making the part in which the conditions in that case are rationalized, and an operation of the crystallization catalyst by the borate is made small, or a borate is moved or evaporated, and it does not exist form Or by classifying a baking object, the mixed powder with which the rates of the borate particle of hBN covering and a boron nitride particle differed variously can be manufactured.

[0022] The mixed powder with which the borate particle, or its particle and boron nitride particle of hBN covering of this invention were contained can be used for the same application as the conventional hBN powder. Especially, since there is little orientation, the borate particle or the mixed powder of this invention is suitable as a filler of the application of the resin which thought thermal conductivity as important, or a rubber constituent, especially the radiator material of electronic parts.

[0023] In the radiator material of this invention, as for the content rate of the mixed powder of the borate particle of hBN covering, or its particle and boron nitride particle, it is desirable that it is 20 to 80 volume %, and, as for rubber, it is desirable that it is addition reaction mold liquefied silicone.

[0024] Next, the borate particle of hBN covering of this invention or the manufacture approach of mixed powder is explained. The big description of this invention is having rationalized the raw material. Namely, it sets to the 3 yuan composition diagram (a melamine, a boric acid, inorganic compound) of the mole percentage of at least a kind of inorganic compound chosen as the melamine, the boric acid, and the list from the hydroxide and carbonate of magnesium and calcium. It is having used as the start raw material mixture which exists within limits surrounded by the line which connects Points A (35, 60, 5), B (25, 70, 5), C (5, 80, 15), and D (5, 5, 90) (refer to drawing 5). Because of the purpose which builds the core section which consists of a borate particle, it is the description that the rate of an inorganic compound is remarkably high, and this has it in the manufacturing technology of the conventional hBN compared with having been stopped to several% or less in consideration of the hBN purity of a final product. [specific]

[0025] Mixing of a raw material is performed using common mixers, such as a ball mill, a ribbon blender, and a Henschel mixer, holds it for 1 to 100 hours under the ambient atmosphere which contains 40-100 degrees C and the steam beyond relative humidity 5% preferably the temperature of 0-200 degrees C, and makes the mixture containing the hydroxide and/or carbonate of a boric-acid melamine (C3N6H6.2H3BO3), magnesium, and/or calcium generate.

[0026] Subsequently, remaining as it is or the mixed powder with which the borate particle and boron nitride particle of hBN covering of this invention were contained under non-oxidizing atmospheres, such as nitrogen and ammonia, by calcinating preferably at the temperature of 1700-2200 degrees C for 2 to 10 hours for 0.5 to 24 hours after casting by the two or less 100 kgf/cm pressure preferably two or less 300 kgf/cm can be manufactured for this mixture.
[0027] And the rate of the borate particle of hBN covering of this invention in mixed powder can be raised by carrying out ultrasonic distribution of this mixed powder into solvents, such as water, and sorting out the sieve top residue with 24micromJIS sieve.
[0028] If crystallization of hBN does not progress that burning temperature is less than 1700 degrees C, but it becomes impossible to fully cover a borate particle front face with hBN and 2200 degrees C is surpassed, the boric acid in a borate will evaporate and it will become difficult to cover a borate with hBN.
[0029]
[Example] Hereafter, an example and the example of a comparison are given and it explains still more concretely.
[0030] It mixed using the Henschel mixer with the compounding ratio which shows examples 1-11, the example 1 of a comparison - 5 boric acids, a melamine, and an inorganic compound in Table 2. it -- the constant temperature of the temperature of 90 degrees C, and 90% of relative humidity -- after holding by the constant humidity in a plane for 6 hours, it cracked lightly with the mortar made from an alumina, and metal mold molding was carried out by pressure 100 kgf/cm2. The crucible made from pBN was filled up with the whole quantity (about 1000g) of molding (diameter [of about 40mm] x height of 15mm), and it calcinated at 2000 degrees C among N2 air current for 2 hours using the high frequency induction furnace.
[0031] After cracking a baking object with the mortar made from an alumina and carrying out a particle size regulation by the 150-micrometer dry type screen, the powder which carried out the particle size regulation if the example 1 was removed subsequently, as it is After carrying out ultrasonic distribution of the powder which carried out the particle size regulation about the example 1 into ethanol further, the peak in which sheet molding is possible was kneaded for the powder which removed less than 24-micrometer fines with the sieve, and was obtained by drying to addition reaction mold liquefied silicone gel (Toshiba Silicone make), respectively. Kneading was performed for 10 minutes using the lab PURASUTO mill. After casting this kneading object by pressure 100 kgf/cm2 on the sheet of 1mm thickness, it vulcanized at 150 degrees C for 1 hour, and pierced in TO-3 mold size.
[0032] After inserting this between the TO-3 mold copper heater case and the copper plate and setting by bolting torque 3 kgf/cm2, thermal conductivity was measured having applied the power of 5W to the heater case.
[0033] Moreover, the above-mentioned powder by which the particle size regulation was carried out to 150 micrometers or less was cast by the pressure of 100 kgf/cm2 in the sample electrode holder (20x18x1mm) for powder X diffractions, powder X diffraction measurement was performed, and OI value was calculated. Those results were summarized in Table 3.
[0034]
[Table 2]

		配合割合 (モル%)		
		無機化合物	メラミン	ホウ酸
実施例	1	水酸化ﾏｸﾞﾈｼｳﾑ：12	28	60
	2	同上 ：12	28	60
	3	同上 ：45	15	40
	4	同上 ：25	15	60
	5	水酸化ｶﾙｼｳﾑ ：12	28	60
	6	同上 ：45	15	40
	7	同上 ：25	15	60
	8	炭酸ﾏｸﾞﾈｼｳﾑ ：12	28	60
	9	同上 ：45	15	40
	10	同上 ：25	15	60
	11	炭酸ｶﾙｼｳﾑ ：12	28	60
比較例	1	水酸化ﾏｸﾞﾈｼｳﾑ： 2	28	70
	2	同上 ：32	28	40
	3	同上 ： 5	15	80
	4	同上 ：65	15	20
	5	同上 ：55	5	40

[0035]
[Table 3]

		熱伝導率(W/m·K)	OI値	備考
実施例	1	3.4	7	図1参照
	2	3.2	11	
	3	2.4	24	
	4	1.8	55	図3参照
	5	2.6	25	
	6	2.0	45	
	7	1.7	72	
	8	2.3	18	
	9	1.8	33	
	10	1.7	45	
	11	1.7	45	
比較例	1	1.0	112	
	2	0.8	358	
	3	0.4	542	
	4	0.6	ND	BN < 20wt%
	5	0.6	ND	同上

[0036] Furthermore, the component by energy dispersion mold fluorescence-X-rays measurement was identified SEM photograph observation of the particle obtained above. Consequently, the boric-acid magnesium (drawing 1 - 2 reference) by which the example 1 was extensively covered by hBN was most. Moreover, in the examples 4, 7, and 10, it was the mixed powder of the borate particle and hBN particle which were partially covered with hBN, and was the mixed powder of the borate particle and hBN particle which were covered almost extensively in the other example by hBN. An example of the SEM photograph of 24-micrometer retained-on sieve particle of the mixed powder obtained in the example 4 was shown in drawing 3 .

[0037] On the other hand, it was what cannot say at all that the examples 1-5 of a comparison are scattering structures as shown in general in drawing 4 excluding a massive particle, and are the borate particles of hBN covering. That is, when the powder manufactured in the examples 1-5 of a comparison was distributed in ethanol and 24-micrometer sieve top residue was observed, it is only a scale-like particle and the massive particle was not found.

[0038]

[Effect of the Invention] According to this invention, the mixed powder of the borate particle with which the hBN primary particle was covered firmly, or a this particle and a hBN particle is offered. The borate particles or the mixed powder of this invention are high temperature conductivity and high insulation, and since there is also little orientation, they are suitable as a filler of the radiator material of electronic parts.

[Translation done.]